Journal of Membrane Science, 46 (1989) 225–241
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

GAS AND SURFACE DIFFUSION IN MODIFIED γ-ALUMINA SYSTEMS

R.J.R. UHLHORN, K. KEIZER and A.J. BURGGRAAF

University of Twente, Department of Chemical Engineering, Laboratory for Inorganic Chemistry, Materials Science and Catalysis, P.O. Box 217, 7500 AE Enschede (The Netherlands)

(Received June 8, 1988; accepted in revised form February 9, 1989)

Summary

The transport of pure gases through a microporous membrane is described. The alumina-based membrane (pores 2.5–4 nm) is suitable for Knudsen diffusion separation. To improve the separation factor, interaction with and mobility on the pore wall of one of the gases of a mixture is necessary. To introduce surface diffusion of oxygen and hydrogen, a γ-alumina membrane was impregnated with silver. If temperature and atmosphere are controlled carefully, finely dispersed silver up to 17% by weight can be introduced. At higher loads and under oxidizing conditions, particle growth occurs. In adsorption experiments, little oxygen adsorption on the silver-modified γ-alumina could be detected. This is due to a decrease in accessible surface area of the silver because of particle growth of silver under oxygen. The mobility of hydrogen on the surface was tested by counterdiffusion experiments, of which the theory is given. Hydrogen shows a considerable mobility on the surface at 293 K. At low pressures the flux ratio of hydrogen to nitrogen improved from 3.8 to 8.8. Magnesia was introduced into the γ-alumina membrane to enhance the adsorption and mobility of CO_2. It is known that 30% of the CO_2 transport on non-modified γ-alumina is surface diffusion. The highest achievable magnesia load was 2.2% by weight. Introduction of magnesia into the γ-alumina surface gives more strong base sites and fewer weak base sites. This results in stronger bonding of CO_2 on the surface, but the amount adsorbed is comparable with the amount of CO_2 adsorbed on non-modified γ-alumina. The contribution of surface diffusion to the total transport decreases with the introduction of magnesia, as is shown by counterdiffusion. The more strongly bonded CO_2 is less mobile, resulting in a smaller surface flux.

1. Introduction

In the past few years, a number of papers have been published concerning the preparation and characterization of microporous ceramic membranes of different materials [1–9]. With γ-alumina, non-supported layers could be obtained with a very narrow pore size distribution around a pore diameter of 2.5 nm and a porosity of 50% [1–2]. The formation of a thin crack-free layer (thickness 1–5 μm) with the same microstructure on a single support and on a multilayer support with larger pores has been described [3,8]. Liquid per-

0376-7388/89/$03.50

meation and separation characteristics were determined and, for instance, a retention above 90% was achieved for poly(ethylene glycol) with a molecular weight of 2000 [4–6]. Research has now focussed on the possible application of these membranes for gas and vapour separation.

Recently the transport of pure gases through a microporous alumina-based membrane has been described [8]. If the pores of a porous medium are smaller than the mean free path of the gas molecules, Knudsen diffusion occurs. Since the Knudsen permeability is directly proportional to the molecular velocity, gases can be separated due to differences in their molecular masses. However, this separation mechanism is only of interest for light gases such as H_2 and He. In order to achieve high separation factors in other systems, different mechanisms have to be employed.

Separation factors can be influenced by introducing an interaction between one of the gases in the mixture and the pore wall. If the adsorbed species is mobile on the surface of the pore, it will diffuse along the surface concentration gradient. The occurrence of this type of transport, called surface diffusion, is frequently reported in porous materials [10–12].

A specific interaction between a gas and the pore can be introduced by chemical modification of separation layers. Thus, the physical and chemical characteristics of the pores are changed, resulting in a decreased pore size and a surface interaction.

In this paper two types of modifications will be described. First, the modification of γ-alumina separation layers with silver is presented, in order to enhance the interaction between oxygen and hydrogen and the pore wall. The occurrence of surface diffusion in this system was determined. The second system studied is γ-alumina modified with magnesia. It is known from previous studies [13] that CO_2 exhibits surface diffusion on γ-alumina. By introducing magnesia, the interaction between CO_2 and the surface can be enhanced. The effect of the modification with magnesia on the surface flow contribution of CO_2 was studied.

2. Theory

2.1 Gas phase flow

In homogeneous porous media with a pore radius larger than 1.5 nm, combined Knudsen and Poiseuille flow occurs. Knudsen diffusion takes place when the mean free path of the molecules is larger than the mean pore radius of the porous medium, while laminar flow takes place when the mean free path of the molecules is smaller than the mean pore radius of the porous medium. For a pure, non-sorbable gas and a homogeneous porous medium, the permeability F_0 (in mol/m^2-sec-Pa) is given by [14]:

$$F_0 = F_{0k} + F_{0p}\bar{P} = \frac{2\epsilon\mu_k \bar{r}\bar{v}}{3RTL} + \frac{\epsilon\mu_p \bar{r}^2}{8\eta RTL}\cdot\bar{P} \tag{1}$$

where F_{0k} is the permeability due to Knudsen diffusion, $F_{0p}\bar{P}$ the contribution due to laminar flow, ϵ is the porosity, $\bar{r}$ the modal pore radius of the medium and μ_k and μ_p are shape factors, generally assumed to be inversely proportional to the tortuosity factor of the porous medium. R is the gas constant per mole, T the temperature, L the thickness of the porous medium, $\bar{P}$ the mean pressure, η the viscosity of the gas and $\bar{v}$ the average molecular speed:

$$\bar{v} = \left(\frac{8RT}{\pi M}\right)^{0.5} \tag{2}$$

where M is the molar mass of the gas.

Permeability is defined as a reciprocal resistance against mass transport through a porous medium. Since a multilayer system can be considered as resistances in series, permeability for such a system is given by:

$$F_0 = \left(\sum_i \frac{1}{F_{0,i}}\right)^{-1} \tag{3}$$

where $F_{0,i}$ is the permeability of layer i. With the help of eqn. (3), the permeability data of a two-layer system can be corrected for the influence of the support [13].

2.2 Surface flow

When pressure and temperature are such that a gas is adsorbed on the surface, account must be taken of the presence of surface flow. Adsorbed molecules may have considerable mobility, resulting in an additional transport along the surface in the direction of decreasing surface concentration.

The mechanism of surface flow is rather complicated and has been treated in many papers [15–17]. For low surface concentrations, the surface flow F_s (mol/m^2-sec) for a pure gas is generally described by the two dimensional form of Fick's law:

$$F_s = -\rho(1-\epsilon)\mu_s D_s \frac{dq}{dl} \tag{4}$$

where ρ is the true density of the medium (kg/m^3), D_s the surface diffusion coefficient (m^2/sec), μ_s the shape factor for surface diffusion and dq/dl the concentration gradient of the adsorbed species; q is the amount adsorbed (mol/kg). From this expression the surface permeability F_{0s} can be determined:

$$F_{0s} = \frac{F_s}{\Delta P} = \frac{\rho(1-\epsilon)D_s\mu_s}{L}\frac{dq}{dP} \tag{5}$$

where ΔP is the pressure difference. The term dq/dP is given by the adsorption isotherm.

To demonstrate the influence of the pore size on the magnitude of the surface flow, eqn. (5) is rewritten considering that:

$$\rho(1-\epsilon)q=\frac{S_v}{A_0 N_{av}}x_s \tag{6a}$$

and

$$S_v=\frac{2\epsilon}{\bar{r}} \tag{6b}$$

where S_v is the surface area (m^2/m^3), A_0 is the surface area occupied by an adsorbed molecule, N_{av} is Avogadro's constant and x_s is the percentage of occupied surface compared with a monolayer. Substituting eqn. (6) in eqn. (5) yields:

$$F_{0s}=\frac{F_s}{\Delta P}=\frac{2\epsilon\mu_s D_s}{\bar{r}A_0 N_{av}}\frac{dx_s}{dP} \tag{7}$$

It can be seen from the above equation that the surface permeability increases with decreasing pore size.

To obtain a complete picture of gas transport in porous media, eqn. (1) for the gas phase flow and eqn. (7) for the surface flow for a pure gas can be added [18]. This gives:

$$F_0=\frac{\epsilon}{k_s^2}\left(c_1\frac{\bar{r}}{M^{0.5}}+c_2\bar{r}^2\frac{\bar{P}}{\eta}+c_3\frac{D_s}{\bar{r}}\frac{dx_s}{dP}\right) \tag{8}$$

with c_1, c_2 and c_3 constants. As can be seen from this equation, surface diffusion becomes more important when pore size is decreased.

To determine whether surface diffusion is present, counterdiffusion is employed. Here, two gases counterdiffuse in an isothermal, isobaric system (Fig. 4A). In this case, flow is absent, since there is no pressure difference. Therefore only diffusion occurs in this kind of systems. If only Knudsen diffusion occurs as gas phase transport mechanism, the flux is given by:

$$F_k=-D_k\frac{dc}{dl} \tag{9a}$$

and

$$D_k=\tfrac{2}{3}\epsilon\mu_k\bar{r}\bar{v} \tag{9b}$$

with dc/dl the concentration gradient. Integration of this equation in the steady-state situation gives the Knudsen permeability F_{0k} in eqn. (1).

When two pure gases counterdiffuse in an isothermal, isobaric system, the

concentrations for gas A and gas B are proportional to their partial pressures, according to the ideal gas law. If the fluxes through the membrane are much smaller than the fluxes along the membrane, the composition of the fluxes along the membrane will remain constant. For pure gases, this means that the partial pressure difference is equal to the pressure of the pure gas. Since counterdiffusion is performed isobarically, the partial pressure difference for each gas is equal to the pressure in the system. Thus, the concentration gradient is proportional to the absolute pressure. Equation (9) then shows that, for counterdiffusion of pure gases, where the flux along the membrane is much larger than the flux through the membrane, the Knudsen diffusion flux increases proportionally to the absolute pressure.

If only gas phase diffusion occurs, the flux ratio of the two counterdiffusing gases is given by:

$$F_A/F_B = (M_B/M_A)^{0.5} \tag{10}$$

with F_A and F_B the flux of gas A and gas B, respectively. When this theoretical ratio cannot be established experimentally, surface diffusion of one of the gases occurs. Owing to surface diffusion, the ratio will deviate from the predicted ratio [eqn. (10)]. In counterdiffusion, however, surface diffusion and gas phase diffusion cannot be assumed to be additive, as is assumed in pure gas transport [eqn. (8)], because momentum will be exchanged between two gases moving in opposite directions. This momentum exchange affects the gas phase flux of both components. Therefore, quantitative prediction of the gas phase flux and the surface flux becomes very complicated [19,20]. Qualitative predictions are possible, however.

3. Experimental

Non-supported γ-alumina separation layers were prepared using a sol/gel technique. Supported γ-alumina separation layers were made using a dipping technique, which employs the capillary force of the porous support [3]. The support (39 mm cross-section, 2 mm thickness) has a porosity of 40% and an average pore diameter of 0.16 μm. Both the supported and the non-supported separation layers have a very sharp pore size distribution around 2.5 nm diameter and a porosity of 50% [4].

Non-supported γ-alumina layers were chemically modified with silver, using a dry or a wet impregnation technique. The chemical modification of γ-alumina separation layers with magnesia was carried out using only the dry impregnation method.

Adsorption experiments for CO_2 on non-modified and modified γ-alumina were carried out using a thermogravimetric method (Cahn balance 2000).

Permeation measurements with CO_2 were carried out using supported sep-

aration layers. The values were corrected for the influence of the support, using the series resistance model.

Counterdiffusion measurements were performed to see if surface diffusion of CO_2 on magnesia-modified and of O_2 and H_2 on silver-modified γ-alumina separation layers occurred. The experiments were performed on non-supported separation layers of 100 μm thickness, employing the well known Wicke–Kallenbach method [21]. The composition of the gas streams was analysed by gas chromatography.

4. Results and discussion

4.1 Synthesis: load

Non-supported γ-alumina separation layers were modified with silver by using three different methods.

1. Non-supported γ-alumina layers were exposed to a 1.5 *M* silver salt and 3 *M* urea impregnation solution [22]. After 2 hr the impregnated system was taken out of the impregnation liquid and allowed to react at 90°C. The urea decomposes, giving hydroxyl groups. These again react with silver ions, forming silver oxide. A further heat treatment at 400°C is necessary to decompose the oxide to silver. This procedure was repeated several times.

2. The same procedure was followed for a 0.06 *M* silver acetate solution. In this case an interaction between the γ-alumina surface and the ions occurs [23]. After 2 hr the γ-alumina layers were taken out of the solution and the adsorbed silver acetate was decomposed to silver at 400°C.

3. The impregnation methods 1 and 2 were repeated, but now the exposure time to the impregnation solution was 2 days for the silver salt/urea solution and 3 days for the silver acetate solution. High loads can be expected, owing to adsorption of the molecules on the pore wall of the γ-alumina. The reaction and decomposition temperatures were the same.

The results of the impregnation are presented in Table 1. The degree of dispersion was investigated by TEM measurements, and the load was determined by titration. The table shows that the highest loads are obtained by employing impregnation for 2 hr with the silver salt/urea solution. When loads of 17% wt are reached, particles start to grow. The dispersion becomes worse as more silver is incorporated.

The critical step in this procedure is the decomposition of silver oxide to silver. It is well known that silver is very mobile on surfaces [28]. In addition to its high mobility, the wettability of silver on the surface of γ-alumina is poor. Therefore silver particles tend to cluster on the surface of γ-alumina, especially when temperature and load are high.

To avoid clustering in the decomposition of the silver oxide, slow heating rates (12°C/hr) are used. The effect of the heating rate on the dispersion is

TABLE 1

Effect of several impregnation methods on load and dispersion of silver in γ-alumina

Method	Impregnation	Load		Dispersion
		% wt	g Ag/g Al_2O_3	
Silver salt + urea	1×	6	0.06	
	4×	11	0.13	particles < 10 nm
	9×	17	0.20	particles < 10 nm
	10×	18	0.21	some particles < 10 nm
	11×	19	0.24	all particles > 10 nm
AgAc	5×	4	0.04	
Silver salt + urea	1× (46 hr)	7	0.08	
AgAc	1× (65 hr)	2.5	0.025	

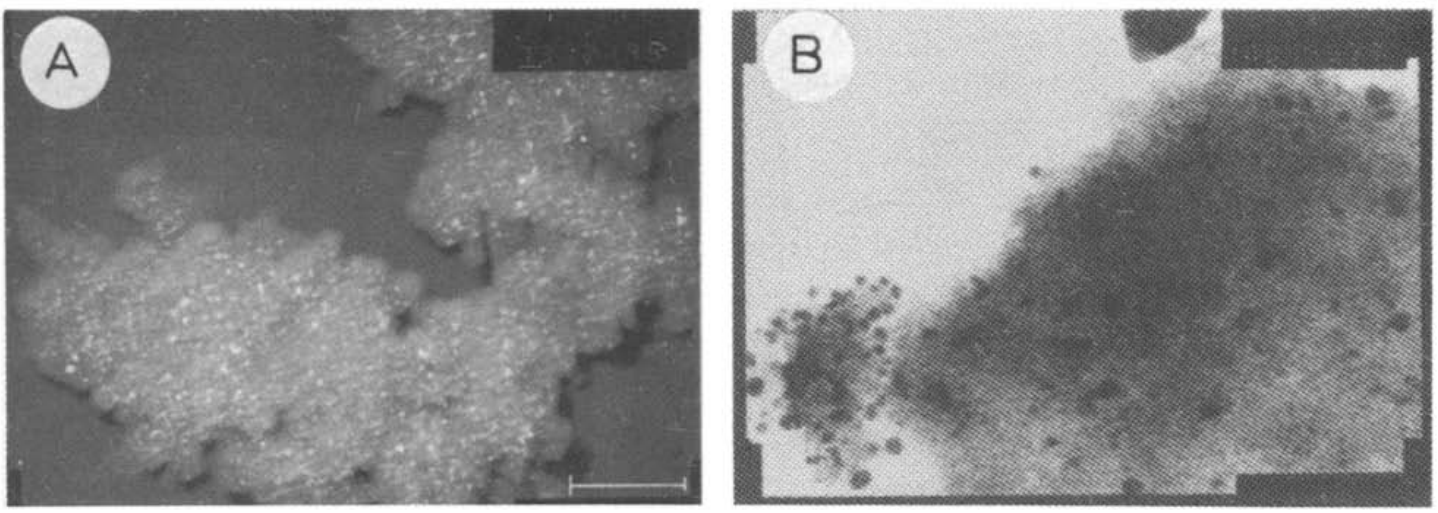


Fig. 1. A. TEM darkfield picture of a non-supported γ-alumina layer modified with 17% wt of silver, slow heating rate, finely dispersed (bar is 100 nm). B. TEM picture of a non-supported γ-alumina layer modified with 17% wt of silver, fast heating rate, finely dispersed (bar is 100 nm).

shown in Fig. 1. A slow heating rate gives finely dispersed silver (Fig. 1A), but a fast heating rate results in poor dispersion (Fig. 1B).

In order to obtain loads above 17% wt and good dispersion, the atmosphere should be changed. All the samples from Table 1 are heat treated in air. In this oxidative atmosphere, silver tends to sinter, and when the load becomes high enough particle growth occurs. When the samples are heat treated in hydrogen, i.e. in a reducing atmosphere, the tendency of silver to sinter is smaller and the dispersion is better maintained. In this way high silver loads with a good dispersion can be obtained [24].

A second modification on non-supported γ-alumina separation layers was performed with magnesia. γ-Alumina shows strong acid–base properties. In-

TABLE 2

Loads after impregnation with a 1 *M* magnesium salt/2 *M* urea solution

Method	Impregnation	Load	
		% wt	g Mg/g Al_2O_3
Magnesium salt + urea	4×	1.0	0.010
	5×	1.7	0.017
	6×	1.9	0.019
	8×	2.0	0.020
	10×	2.3	0.023
	12×	2.4	0.025

troduction of magnesia causes a change in these properties [25–27], which will also change the adsorption and surface diffusion behaviour of CO_2.

The method employed for the magnesia impregnation was based upon the results of the silver impregnations. Thus, non-supported γ-alumina separation layers were impregnated with a 1 *M* magnesium salt and 2 *M* urea solution for 2 hr, allowed to react at 90 °C and thermally treated at 400 °C to give magnesium oxide. The loads, as determined by AAS, are given in Table 2. As the loads are low and the mobility of magnesia is negligible in comparison with that of silver, no dispersion analysis was done.

After ten impregnation cycles, the load of magnesia is $9.47\text{–}10^{-4}$ mol/g Al_2O_3 (Table 2), and the load of silver after ten impregnation cycles is 1.95×10^{-3} mol/g Al_2O_3 (Table 1). The silver load is about twice the magnesia load, although the concentration of silver in solution was only 1.5 times the concentration of magnesium in solution. The difference must be explained in terms of reaction kinetics. First results indicate that the reaction of silver and urea is much faster than that of magnesium and urea. Therefore more silver is deposited in the pores, resulting in higher loads.

All the preceding impregnation experiments were carried out using non-supported γ-alumina separation layers. In further research, the loading of supported system was investigated. First results indicate that the presence of the support leads to higher loads.

4.2 Interaction: adsorption

Adsorption experiments were performed on three different systems. The O_2 adsorption on silver-modified non-supported γ-alumina separation layers was determined. Also, CO_2 adsorption on non-modified non-supported γ-alumina separation layers was determined. These results were published earlier [13] and will only be briefly mentioned. Lastly, the CO_2 adsorption on the same non-supported γ-alumina separation layers, but modified with magnesia, was measured. Results will be presented in this section.

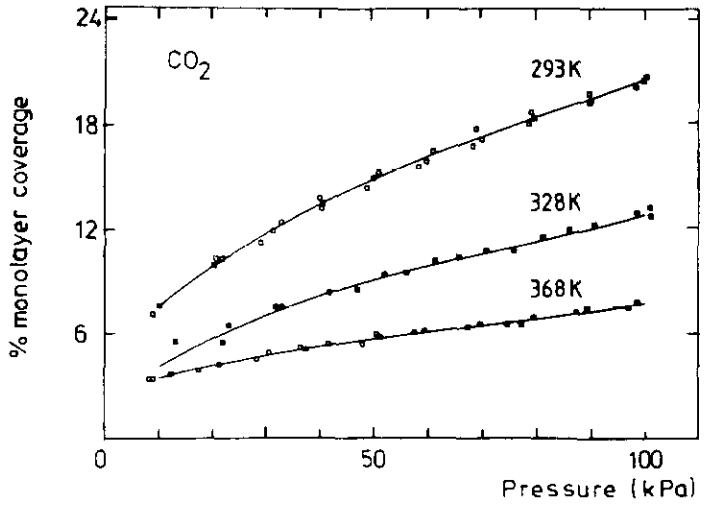


Fig. 2. Adsorption isotherms of carbon dioxide on non-supported γ-alumina layers ($\epsilon=50\%$, $S_v=1.1\times10^9\ m^2/m^3$) at several temperatures.

Adsorption experiments with oxygen at 100°C were performed on silver-modified non-supported γ-alumina layers (17% wt of silver). No oxygen adsorption on these modified γ-alumina layers was found. This conflicts with the literature [29], where oxygen adsorption is found on silver.

The reason for this contradiction is the atmosphere. As shown in the previous section, silver sinters readily under oxidizing conditions. The adsorption experiments were carried out under oxygen at 120°C with samples loaded with 17% wt of silver. It can be expected that under these circumstances rapid particle growth will occur. This leads to a reduction of the accessible surface area for oxygen adsorption, and the amount of oxygen adsorbed becomes so small that detection is no longer possible.

The adsorption of CO_2 on non-supported γ-alumina layers was determined. Figure 2 gives the adsorption isotherms at several temperatures. From these data the isosteric heat of adsorption can be determined using the Clausius–Clapeyron-type equation:

$$E_{st} = -R\left[\frac{\delta \ln P}{\delta(1/T)}\right]_q \tag{11}$$

The results are summarized in Table 3. A mean value of 25 kJ/mol is calculated for E_{st}, which is a characteristic value for physisorption or weak chemisorption. It is generally accepted that the activation energy for surface flow and the heat of adsorption are coupled [10–12], the ratio being 0.3 to 0.5. This implies an activation energy for surface flow of 8–12 kJ/mol, and it can be expected that part of the adsorbed molecules will be mobile on the surface.

The adsorption isotherms of Fig. 2 are reversible. This means that, if the pressure is lowered and desorption occurs, the equilibrium situation is the same as for adsorption.

The non-supported γ-alumina layers were modified with magnesia to enhance the adsorption and mobility of CO_2, as described in the previous section.

TABLE 3

Some examples of the calculation of the isosteric heat of adsorption of CO_2 on non-supported γ-alumina layers

Occupation ($\times 10^{-2}$)	T_1 (°C)	T_2 (°C)	E_{st} (kJ/mol)
7.3	55	95	26.3
7.9	20	95	26.3
7.9	55	95	25.4
8.7	20	55	25.6

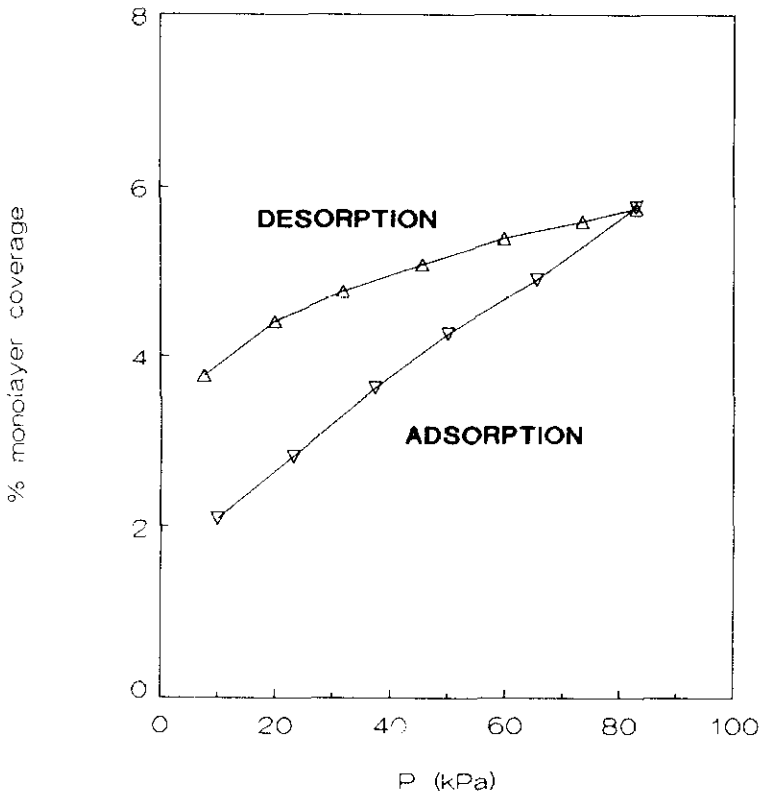


Fig. 3. Adsorption and desorption branch of carbon dioxide on non-supported γ-alumina layers, modified with 2.2% wt of magnesia at 101 °C.

Figure 3 represents the adsorption of CO_2 on a magnesia-modified alumina system at 101 °C. The load in this case was 2.2% wt MgO (Table 2). The adsorption part gives the equilibrium value of the amount of adsorbed CO_2 when the pressure is increased from zero to 1 bar. At 101 °C between 10 and 90 kPa, the surface concentration of CO_2 increases to 6% of a monolayer coverage. It can be calculated for this situation that the amount adsorbed is equal to 0.15 mol/kg membrane material. For the non-modified material under the same conditions, the amount adsorbed between 10 and 90 kPa is also 0.15 mol/kg; it can thus be seen that the adsorption is not increased by the modification with magnesia.

The status of the adsorbed species, however, has changed significantly. This can be seen from the desorption part in Fig. 3. After the modification with

magnesia, the adsorption and desorption curves show a hysteresis, whereas the adsorption on the non-modified material is reversible. For the modified material at 101 °C about half of the adsorbed CO_2 is not desorbed when the pressure is lowered. At lower temperatures, the amount that desorbs becomes even smaller.

The irreversible adsorption of CO_2 on the magnesia-modified material must be due to strong bonding of the CO_2 on the modified γ-alumina surface. CO_2 is known to react as an acidic gas to form monodentate and bidentate species [25]. Therefore the amount of strong base centres must have been increased by introducing magnesia, resulting in a much stronger bonding of CO_2. Because the total amount adsorbed is the same before and after modification, the amount of weak base centres must have decreased to balance the increased strong base centres. This is in accordance with recent literature studies [27], which indicate that introduction of magnesia leads to an increase in the number of strongest base centres and to a decrease in base sites of moderate strength.

4.3 Mobility: surface diffusion

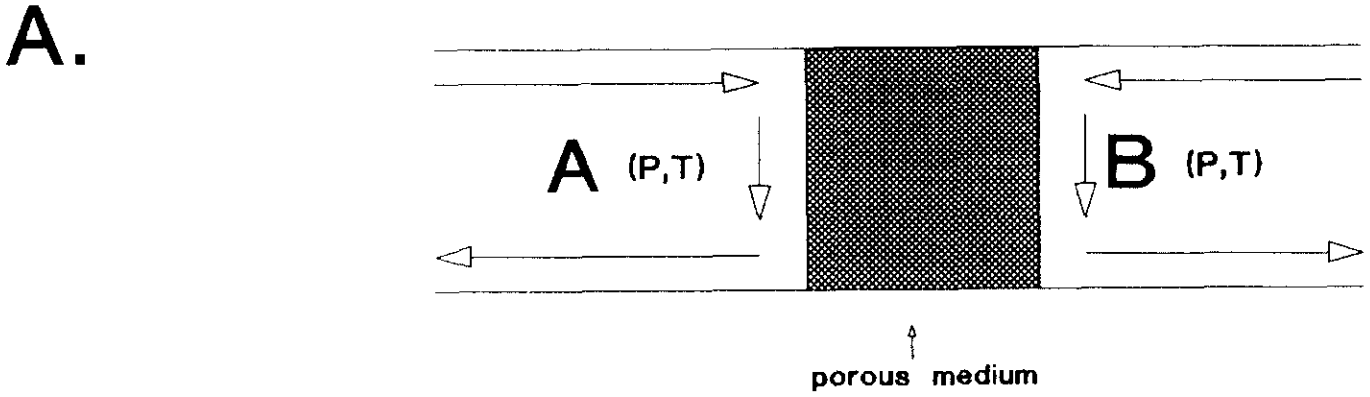
Two parameters are important in order to have surface diffusion. First, one of the gases has to interact with the pore wall, and second, this gas has to be mobile on the surface of the pore wall. A discussion of this mobility of the adsorbed species on the pore wall will be given below.

To determine surface diffusion, in principle three methods are suitable. The first is permeation with pure gases, from which one can determine the ratio of the permeabilities (so-called permselectivity). Second, one can use counterdiffusion measurements, where two gases counterdiffuse in an isobaric and isothermal system. The third suitable method is a separation experiment, where the increase in separation efficiency is determined. Only the first two approaches will be discussed here.

The mobility of oxygen and hydrogen on silver-modified non-supported γ-alumina layers was determined by counterdiffusion, employing the well-known Wicke–Kallenbach method [21]. Figures 4 and 5 present flux ratios of O_2 and N_2, and H_2 and N_2, at 20 °C as a function of mean pressure. Nitrogen is the inert gas. The silver load is 17% by weight. The dashed line gives the theoretical ratio of the fluxes if no surface diffusion occurs. This ratio can be calculated from eqn. (10).

For oxygen and nitrogen, the theoretical ratio is 0.94. From Fig. 4 it can be seen that the experimental flux ratio is close to the theoretical ratio. This means that only gas phase diffusion occurs and no surface diffusion is present, in accordance with the adsorption experiments. No adsorption could be detected, owing to a decrease in accessible surface area under oxidizing conditions, so surface diffusion is not possible.

Figure 5 gives the theoretical and experimental flux ratio for hydrogen and nitrogen on a silver-modified γ-alumina layer. The hydrogen flux is higher than



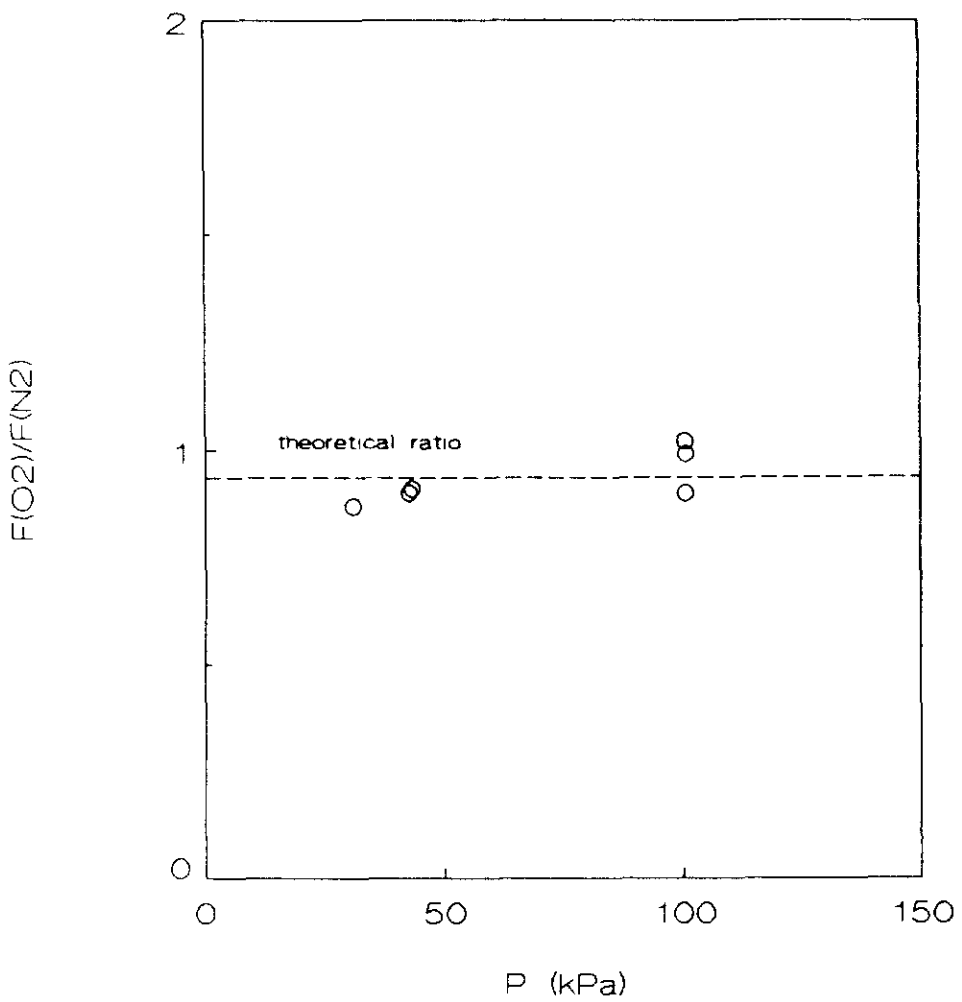


Fig. 4. A. Configuration of counterdiffusion of pure gases in an isothermal, isobaric system. B. Experimental (symbol ○) and theoretical flux ratio of oxygen and nitrogen at 20°C on a non-supported γ-alumina layer, modified with 17% wt of silver, measured in counterdiffusion configuration.

predicted from theory, which implies that hydrogen is mobile on the silver surface and surface diffusion occurs.

The experimental flux ratio decreases with increasing pressure. This can be explained with the help of eqns. (7) and (9). As the amount of adsorbed hydrogen as a function of pressure becomes constant (as expected from adsorption theory), then it follows from eqn. (7) that the surface diffusion flux of hydrogen becomes constant. The gas phase flux, however, increases with increasing pressure, as indicated by eqn. (9). Thus, the ratio between the surface

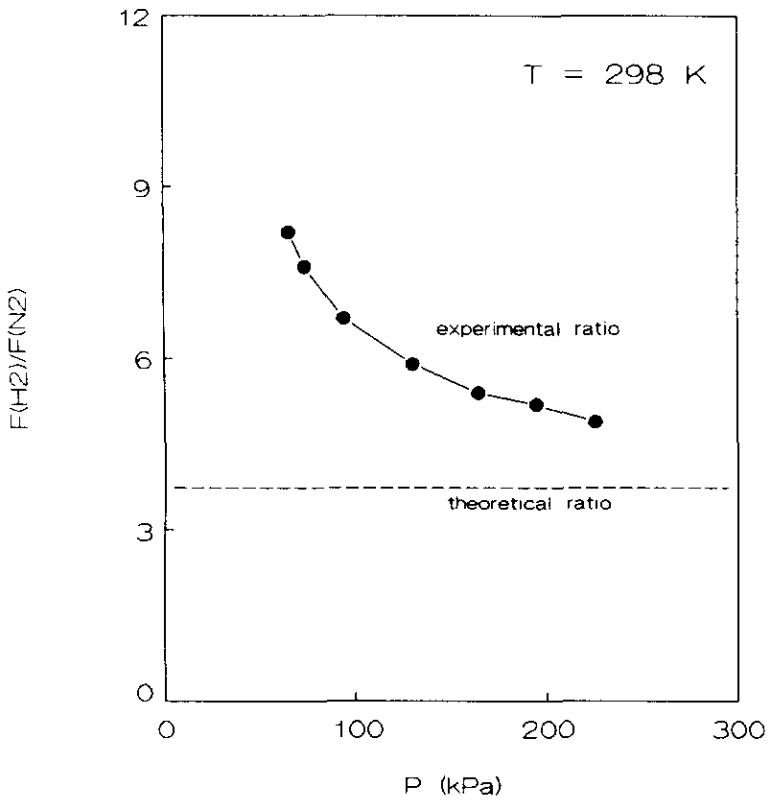


Fig. 5. Experimental (symbol ●) and theoretical flux ratio of hydrogen and nitrogen at 25 °C on a non-supported γ-alumina layer, modified with 17% wt of silver, measured in counterdiffusion configuration.

flux and the gas phase flux decreases with increasing pressure, resulting in the negative slope of the flux ratio shown in Fig. 5.

Permeation and counterdiffusion measurements with CO_2 at room temperature were performed on non-modified non-supported γ-alumina separation layers [13]. They indicated the presence of surface diffusion of CO_2 on the γ-alumina surface. Both permeation and counterdiffusion experiments showed a surface flux contribution of about 30% of the total flux.

Counterdiffusion measurements with N_2 and CO_2 were also performed on 100 μm thick magnesia-modified non-supported γ-alumina layers at 20 °C as a function of pressure. Nitrogen served as the inert gas in this experiment. The magnesia load was 2.2% wt. Results are given in Fig. 6. The dashed line again represents the theoretical permeability ratio (0.80). The measured ratio is significantly higher, indicating the presence of surface diffusion. From a comparison of lines 1 and 2 in Fig. 6, however, it can be seen that the contribution of the surface flux to the total flux decreases after the introduction of magnesia into the system, although surface flow is still present. This is in accordance with the adsorption experiments. On the γ-alumina–magnesia surface, more strong base centres and fewer weak base centres are present than on the γ-alumina surface. The activation energy of migration for the CO_2 bonded to the strong base centres is so high that this CO_2 is not mobile. Therefore the surface contribution decreases, resulting in lower permeability ratios than measured on a γ-alumina system.

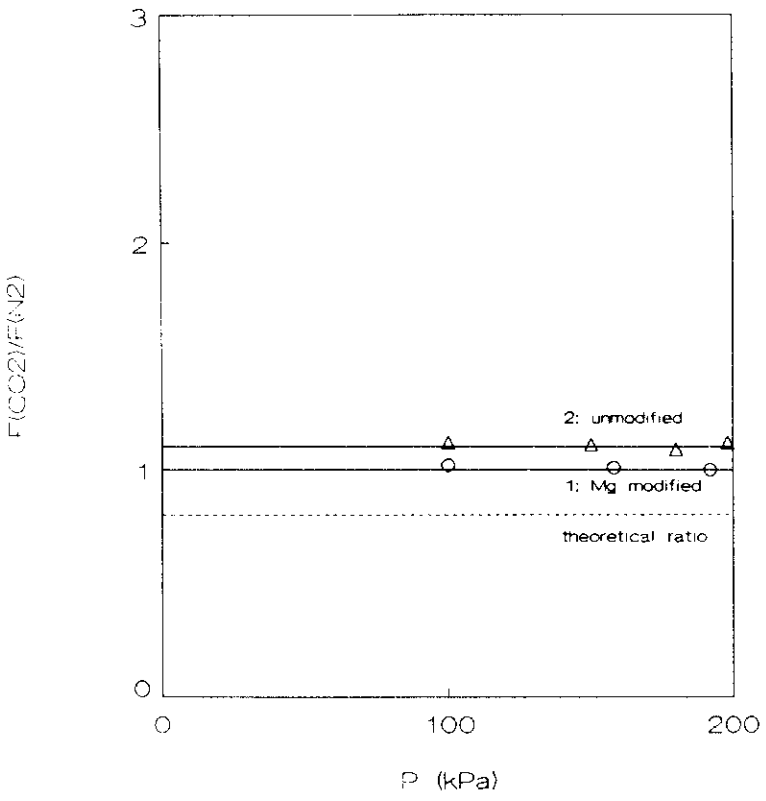


Fig. 6. Experimental and theoretical flux ratio of carbon dioxide and nitrogen at 20 °C on: 1, non-supported γ-alumina layers, modified with 2.2% wt of magnesia; 2, non-supported γ-alumina layers, non-modified, measured in an isothermic and isobaric system (counterdiffusion).

An increase of the contribution of the surface flux to the total gas phase flux can be obtained only by a further decrease of the pore radius, as indicated in eqns. (7) and (8). This will decrease the gas phase flux and increase the surface diffusion flux, thus improving separation.

5. Conclusions

Non-supported and supported γ-alumina separation layers have been prepared. They were modified with silver to enhance surface flow of oxygen and hydrogen, and with magnesia to increase the surface diffusion of CO_2, which also exists on non-modified γ-alumina.

With a technique of impregnation with a solution of a silver salt and urea, it is possible to load γ-alumina separation layers with 17% wt of silver. By careful manipulation of temperature treatment, a good dispersion can be maintained. The same technique was applied in the modification of γ-alumina separation layers with magnesia, resulting in a highest achievable load of 2.2% wt.

Adsorption of O_2 could not be detected with a thermogravimetric method. In line with this, no surface diffusion of O_2 was found on silver-modified γ-alumina separation layers. Most likely this is due to sintering of the silver under oxidizing conditions.

Hydrogen showed considerable mobility on silver-modified γ-alumina separation layers. The flux ratio in counterdiffusion measurements with N_2 as

inert gas was 3 times higher than expected. Under a reducing atmosphere, the silver dispersion is maintained, resulting in high surface flow contributions to the overall transport.

Modification of γ-alumina separation layers with magnesia leads to a partially irreversible adsorption of CO_2 on the surface, while adsorption on γ-alumina is reversible. The introduction of magnesia leads to more strong base centres and fewer weak base centres, resulting in more strongly bonded CO_2. A decrease in CO_2 mobility after introduction of the magnesia was detected with counterdiffusion measurements. Since the activation energy of migration is directly coupled to the adsorption energy, this is in accordance with the adsorption behaviour.

Acknowledgements

We thank F.P. Cuperus and R.J. van Vuren for carrying out some of the experiments. The financial assistance of the I.O.P.-membranes is gratefully appreciated.

List of symbols

A	outer surface (m^2)
A_0	surface area of an adsorbed molecule (m^2)
c	concentration (mol/m^3)
D_s	surface diffusion coefficient (m^2/sec)
D_k	Knudsen diffusion coefficient (m^2/sec)
E_{st}	isosteric heat of adsorption (kJ/mol)
F	flux (mol/m^2-sec)
F_k	flux due to Knudsen diffusion (mol/m^2-sec)
F_0	total permeability of gas (mol/m^2-sec-Pa)
F_{0k}	permeability due to Knudsen diffusion (mol/m^2-sec-Pa)
F_{0p}	permeability divided by pressure due to laminar flow (mol/m^2-sec-Pa^2)
F_{0s}	permeability due to surface diffusion (mol/m^2-sec-Pa)
F_s	surface flux (mol/m^2-sec)
$(k_s)^2$	tortuosity factor for surface diffusion (−)
L	thickness of the membrane system (m)
M	molar mass of gas molecules (kg/mol)
N_{av}	Avogadro's constant (mol^{-1})
$\bar{P}$	mean pressure (Pa)
ΔP	pressure difference across the membrane system (Pa)
q	gas amount adsorbed (mol/kg)
R	gas constant (=8.315 J/mol-K)
$\bar{r}$	modal pore radius of the solid medium (m)

S_v surface area of solid system per unit of volume (m^2/m^3)
T absolute temperature (K)
$\bar{v}$ mean molecular speed (m/sec)
x_s fraction of surface covered by adsorbed molecules (–)

Greek letters

ϵ porosity of the membrane system (–)
η viscosity of the gas (N-sec/m^2)
ρ true density of the solid medium (kg/m^3)
μ_k shape factor for Knudsen diffusion (–)
μ_p shape factor for laminar flow (–)
μ_s shape factor for surface diffusion (–)

References

1 K. Keizer, A.F.M. Leenaars and A.J. Burggraaf, The preparation and characterization of porous alumina membranes, Sci. Ceram., 12 (1983) 101–106.
2 A.F.M. Leenaars, K. Keizer and A.J. Burggraaf, The preparation and characterization of alumina membranes with ultrafine pores. Part 1. Microstructural investigations on non-supported membranes, J. Mater. Sci., 19 (1984) 1077–1088.
3 A.F.M. Leenaars and A.J. Burggraaf, The preparation and characterization of alumina membranes with ultrafine pores. Part 2. The formation of supported membranes, J. Colloid Interface Sci., 105 (1985) 27–40.
4 A.F.M. Leenaars and A.J. Burggraaf, The preparation and characterization of alumina membranes with ultrafine pores. Part 3. The permeability for pure liquids, J. Membrane Sci., 24 (1985) 245–261.
5 A.F.M. Leenaars and A.J. Burggraaf, The preparation and characterization of alumina membranes with ultrafine pores. Part 4. Ultrafiltration and hyperfiltration experiments, J. Membrane Sci., 24 (1985) 261–271.
6 A.F.M. Leenaars, K. Keizer and A.J. Burggraaf, Permeability and separation characteristics of porous alumina membranes in reverse osmosis and ultrafiltration, in: S. Sourirajan and T. Matsuura (Eds.) Reverse Osmosis and Ultrafiltration ACS Symp. Ser. No., 281, American Chemical Society, Washington, DC, 1985, pp. 57–68.
7 K. Keizer, A.F.M. Leenaars and A.J. Burggraaf, Inorganic, porous membranes, preparation, structure and potential applications, in: H. Krockel M. Merz and O. van der Biest (Eds.), Ceramics in Advanced Energy Technologies, Reidel, Dordrecht, 1984, pp. 367–386.
8 R.J. van Vuren, B. Bonekamp, R.J.R. Uhlhorn, K. Keizer, H.J. Veringa and A.J. Burggraaf, Formation of ceramic alumina membranes for gas separation, in: P. Vincenzini (Ed.), High Tech Ceramics, Mater. Sci. Monogr., Elsevier, Amsterdam, 1987, pp. 2235–2246.
9 R.J.R. Uhlhorn, M.H.B.J. Huis in 't Veld, K. Keizer and A.J. Burggraaf, New ceramic membrane materials for use in gas separation applications, Sci. Ceram., 14 (1988) 551–557.
10 E.R. Gilliland, R.F. Baddour, G.P. Perkinson and K.J. Sladek, Diffusion on surfaces. I. Effect of concentration on the diffusivity of physically adsorbed gases, Ind. Eng. Chem. Fundam., 13 (1974) 95–99.

11 K.J. Sladek, E.R. Gilliland and R.F. Baddour, Diffusion on surfaces. II. Correlation of diffusivities on physically and chemically adsorbed species, Ind. Eng. Chem. Fundam., 13 (1974) 100–105.

12 H. Tamon, S. Kyotani, H. Wada, M. Okazaki and R. Toei, Surface flow phenomenon of adsorbed gases on activated alumina, J. Chem. Eng. Jpn., 14 (1981) 136–141.

13 K. Keizer, R.J.R. Uhlhorn, R.J. van Vuren and A.J. Burggraaf, Gas separation mechanisms in microporous modified γ-alumina membranes, J. Membrane Sci., 39 (1988) 285–300.

14 U. Eickmann and U. Werner, Gastrennung mit Porenmembranen, Chem.-Ing.-Tech., 56 (1984) 720–721.

15 R.L. Rowell, S.A. Carrano, A.J. deBethune and A.P. Malinauskas, Gas and vapor permeability, J. Colloid Interface Sci., 37 (1971) 242–246.

16 R.W. Tock and K. Kammermeyer, Temperature–separation factor relationships in gaseous diffusion, AIChE J. 15 (1969) 715–718.

17 K. Haraya, Y. Shindo, T. Hakuta and H. Yoshitome, Separation of H_2–CO_2 mixtures with porous glass membranes in the intermediate flow region, J. Chem. Eng. Jpn., 19 (1986) 186–190.

18 R.D. Present and A.J. deBethune, Separation of a gas mixture flowing through a long tube at low pressure, Phys. Rev., 75 (1949) 1050–1057.

19 W.K. Bell, Interactions between a mobile adsorbed phase and diffusing gases in porous media, Ph.D. Thesis, University of Colorado, 1971.

20 M. Asaeda, Combined surface and gas phase diffusion through plugs of porous adsorbent in transition diffusion region, J. Chem. Eng. Jpn., 14 (1981) 1–13.

21 E. Wicke and R. Kallenbach, Surface diffusion of carbon dioxide in activated charcoals, Kolloid-Z., 97 (1941) 135.

22 K.P. de Jong and A.W. Geus, Structural aspects of supported monometallic and bimetallic catalysts, Ph.D. Thesis, University of Utrecht, 1982.

23 Reports of the TAP project, University of Amsterdam, 1979–1980.

24 V.T. Zaspalis, W.P. van Praag, K. Keizer and A.J. Burggraaf, Synthesis and characterization of (modified) Al_2O_3/TiO_2 ceramic membranes for use in catalytic reactions, J. Mater. Sci., (to be published).

25 J.A. Lercher, C. Colombier and H. Noller, Acid–base properties of alumina magnesia mixed oxides. part IV. Infrared study of adsorption of carbon dioxide, J. Chem. Soc., Faraday Trans. I, 80 (1984) 949–959.

26 H. Vink, Diskussion der sauren und basischen Eigenschaften von MgO–Al_2O_3, MgO–SiO_2 und Al_2O_3–SiO_2 Mischoxiden, Z. Phys. Chem., 120 (1980) 119.

27 W. Kania and K. Jurczyk, Acid–base properties of modified γ-alumina, Appl. Catal., 34 (1987) 1–12.

28 L. Lefferts, Factors controlling the selectivity of silver catalysts for methanol oxidation, Ph.D. Thesis, University of Twente, 1987.

29 G.K. Boreskov, I.V. Lokhaova and A.V. Khasin, Adsorption isotherm of oxygen on silver, React. Kinet. Catal. Lett., 16 (1981) 167.